

# Carbon-Rich Ceramic Composites from Ethynyl Aromatic Precursors

(NASA-TM-88812) CARBON-RICH CERAMIC  
COMPOSITES FROM ETHYNYL AROMATIC PRECURSORS  
(NASA) 13 p CSCI 11D

N86-29908

Unclas

G3/24 43568

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Prepared for the  
Tenth Annual Conference on Composites and  
Advanced Ceramic Materials  
sponsored by the American Ceramic Society  
Cocoa Beach, Florida, January 19-24, 1986



# CARBON-RICH CERAMIC COMPOSITES FROM ETHYNYL AROMATIC PRECURSORS

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## SUMMARY

A number of polyfunctional aromatic acetylenes thermally polymerize at low temperatures (180 °C) and pyrolyze with >90 char yield. In nonoxidizing environments, they are thermally stable to 1450 °C. These monomers were chosen as the basis of a model system to study the fabrication and mechanical properties of a continuous filament ceramic matrix composite. Composites were fabricated from aryl poly(acetylenes), SiC particulate filler and graphite, Avco SiC, Nicalon and Nextel fibers. Microstructure, physical and mechanical properties are reported.

## INTRODUCTION

Fiber reinforcement of a ceramic matrix offers the potential for a high temperature material with decreased flaw sensitivity, and hence greater reliability than generally is observed for monolithic ceramics. The fiber can act as a crack deflector providing a mechanism for energy dissipation; it also can bridge matrix cracks, maintaining the load bearing capability of the material and suppressing catastrophic failure. Fabrication of a reinforced ceramic, however, requires low temperatures such that the fiber and fiber/matrix interface are not degraded during processing.

The use of polymeric precursors to a ceramic matrix provides for low temperature processing and extensive control of rheology in infiltration of fiber tows or preforms. The composite can be formed by methods analogous to the fabrication of resin matrix composites, and then pyrolyzed to yield a ceramic char. In order to eliminate the need for repeated impregnation and pyrolysis cycles, it is desirable for the polymer to exhibit a high char yield, minimal dimensional shrinkage or cracking on pyrolysis, and a low melt viscosity for ease of fiber infiltration.

A number of silicon/carbon and silicon/carbon/nitrogen containing polymers recently have been reported in the literature (refs. 1 to 10) as potential precursors to ceramics. The majority of these are not available in sufficient quantity to study composite fabrication and properties, and/or undergo considerable shrinkage on pyrolysis, suggesting the need for repeated reimpregnation. However, a number of di- and trifunctional aromatic acetylenes (fig. 1) are commercially available which thermally homo- and copolymerize to form thermosets (shown schematically in fig. 2) having char yields of >90 percent when pyrolyzed in nonoxidizing environments. These were chosen as the basis for a model system to study the fabrication and mechanical properties of a continuous filament reinforced, brittle carbon matrix from polymeric precursors.

Since the system under discussion here is to serve as a model for silicon-containing polymer systems which are assumed to have lower char yields than the ethynyl aromatics, a particulate ceramic filler was incorporated which might

minimize matrix shrinkage and cracking, and which eventually could be used to control the coefficient of expansion of the final composite for purposes of achieving compatibility with a coating, if necessary, for environmental protection. The particulate filler also might serve as a reactant in a subsequent, higher temperature processing step; for example, a silicon powder could be used to react with excess carbon in the matrix to yield SiC and C, provided that reaction at the fiber interface can be precluded (i.e., the fiber surface is not carbon rich).

Composites were fabricated from ethynyl aromatic monomers, SiC powder, and a variety of fibers including Celion 6000, Celion 3000, Nicalon, Avco SCS-0 and Avco SCS-6 and Nextel 312. The addition of a silsesquioxane additive (Dow Corning A57 paint additive) also was studied.

Composites were characterized by thermogravimetric analysis (TGA), optical and scanning electron microscopy, three-point bending and uniaxial and  $\pm 45^\circ$  tension.

## EXPERIMENTAL

4, 4'-diethynyldiphenylmethane (DEDPM) was purchased from Chem Biochem Research, Inc., Salt Lake City, Utah. The monomer was >90 percent the 1,4 para isomer and was shown by reversed phase chromatography to contain other isomers as well. The monomer was used without further purification.

Unsize Celion, a polyacrylonitrile derived graphite fiber, was obtained from CCF, Inc. Unsize Nextel 312 (boria-alumina-silica) fiber was supplied by 3M Corporation. Nicalon NLM, both regular and ceramic grade, was purchased from Dow Corning. SCS-0 and SCS-6 were obtained from Avco.

The SiC powder was Starck A10 Type 1 alpha phase SiC, having an average particle size of 1.5  $\mu\text{m}$  and surface area of 6 to 7  $\text{m}^2/\text{g}$ .

Polymerization kinetics of DEDPM were determined by a combination of isothermal and scanning DSC techniques. Pyrolysis kinetics of SiC filled DEDPM with Celion 6K were determined by TGA carried out at heating rates of 1 to 15  $^\circ\text{C}/\text{min}$ . Details of the kinetics studies and kinetics parameters have been reported previously (refs. 11 and 12).

The DSC and TGA kinetics results were used to establish a composite processing cycle of 180  $^\circ\text{C}$  polymerization at 200 psi for 1.5 and 1 hr, 350 $^\circ$  post-cure and 3 hr, 600  $^\circ\text{C}$  pyrolysis.

Monomer was dissolved in either acetonitrile or dimethylformimide (DMF) and SiC powder added. For those mixtures in which a silsesquioxane (Dow Corning A57) was used, the A57 was mixed with the solvent prior to addition of monomer or ceramic powder. Fiber was filament wound and coated with the monomer/powder suspension and the solvent evaporated. The prepreg was then cut and stacked in a matched metal die and hot pressed.

Flexural properties were determined in three point bending on unidirectional specimens 6.35 mm wide and minimally 2.2 mm thick at a span to depth ratio of 32:1. Tensile measurements were made on 12.2 mm wide, straight

edge specimens having a gauge length of 12.7 cm. Tapered, glass/epoxy tabs were bonded to the tensile specimens. Strain was determined from gauges bonded to both sides of each specimen.

## RESULTS AND DISCUSSION

DEDPM melts at 60 °C to a low viscosity liquid. Polymerization is highly exothermic, with a heat of reaction of approximately 1200 J/g (fig. 3). The polymer can be cured at 180 °C, and further crosslinked by postcuring at approximately 350 °C, as shown by the increase in shear modulus,  $G'$ , on heating above the cure temperature (fig. 4). On pyrolysis in an inert atmosphere (nitrogen), the composite maintains >94 percent of its initial weight, with the largest weight loss occurring at 500 to 600 °C (fig. 5). A smaller (<0.5 percent) additional weight change is observed at >750 °C.

Differential thermal analysis (DTA) traces of the as polymerized material (fig. 6) exhibited a small exotherm at >330 °C, attributed to postcuring, a larger peak at 600 °C, and several overlapping peaks between 700 and 1100 °C. However, DTA scans of a composite which had been postcured at 350 °C for 1 hr and pyrolyzed at 600 °C for 3 hr contained no peaks between ambient temperature and 1400 °C when heated in argon or nitrogen at 20 °C/min (fig. 6).

Composites fabricated from SiC powder filled DEDPM at a ratio of 2:1 SiC/DEDPM by weight, and Celion 6K showed a "layered" microstructure (fig. 7) in which each ply remained distinct. Layers rich in fiber and DEDPM resin were separated by matrix-rich regions of DEDPM and SiC, the SiC powder appearing to be filtered by the fiber tow. Within the fiber-rich layers matrix regions could be observed which seemed to contain only resin with no SiC particles. The fiber-rich regions also contained a number of voids.

On pyrolysis at 600 °C <3 percent linear shrinkage was observed. Only a few scattered matrix cracks were noted, these were found in the fiber rich region and were perpendicular to the thickness direction (fig. 8).

Flexural testing of the Celion 6000/DEDPM/SiC composites cast from acetonitrile demonstrated a tendency to fail in shear, which was attributed to the "layered" microstructure. Several approaches were used to try to achieve a more uniform microstructure, including the addition in several concentrations of a wetting agent, A57, and the substitution of dimethylformimide for acetonitrile as the solvent used in fabrication. Flexural strengths of these composites are summarized in table I. The acetonitrile/0.42 percent A57 by volume composition was chosen for further study from the combinations examined based on the observations of tensile failure in the flexural specimens and highest flexural strength. The composites cast from DMF, while having almost the same flexural strength as those cast from acetonitrile, required vacuum removal of the solvent, and left the possibility that even then not all solvent had been removed.

Incorporation of the A57 wetting agent improved fiber coating and prepreg handling. The microstructure, however, was quite similar to that observed previously (fig. 8). Some microphase segregation within the matrix near the fiber-rich regions was observed by optical microscopy. Scanning electron microscopy of polished cross sections showed an increased tendency for SiC particles to "pull out" of the matrix on polishing in those laminates which



contained wetting agent, indicating a decrease in bonding between the polymer matrix and SiC particulate with A57 addition. It is assumed that this change in bonding reduces the modulus of the particulate rich layers, diminishing the tendency toward shear failure in the flexural specimens, hence increasing flexural strength (table I).

Two further approaches were attempted to improve microstructural homogeneity. The concentration of filler was reduced from a 2:1 weight ratio of SiC to DEDPM to 1.6:1, with no change in flexural strength. In addition, the tow size of the Celion fiber was reduced from 6000 to 3000 filaments. This diminished the width of the fiber layers, but did not eliminate the layered microstructure (fig. 9).

Tensile specimens were fabricated using Celion 3K, SiC/DEDPM in a ratio of 1.6 to 1, and 0.5 percent A57 by volume in acetonitrile (17 ul of A57 in a 7.62 by 20 by 0.2 cm laminate). Unidirectional specimens showed almost no matrix cracking on pyrolysis (fig. 8). However, the  $\pm 45^\circ$  laminates exhibited considerable cracking in the fiber rich layers as a result of the mismatch in thermal expansion between the SiC filled regions between the layers and deficiency of SiC particles within the fiber tow (fig. 10).

A typical stress-strain curve for the unidirectional laminates is shown in figure 11. Brittle fracture is observed, with no reloading of the fiber indicative of crack bridging subsequent to matrix failure. Tensile properties are summarized in table II. The strength following pyrolysis is 45 to 50 percent that of the as-fabricated composite, and parallels a similar decrease in the strain-to-failure. If one takes the shear strength as half the tensile strength in a  $\pm 45^\circ$  laminate (13), it can be seen that the material is extremely weak in shear (approximately 2 ksi).

It is hoped that a more uniform microstructure (one without the "layered" plies) would have higher shear strength. Composites fabricated with the Avco SCS-6 fiber showed a more uniform microstructure, but extremely poor bonding between the DEDPM matrix and the fiber. Carbon coating of the SiC fiber improved the fiber matrix interface, however, a quantity of fiber sufficient for mechanical property evaluation was not available.

Composites containing Nextel 312 with 390 filaments/tow had a more uniform microstructure (fig. 12). These fibers are elliptical in cross section, as contrasted with the circular Celion, and do not have the tendency to close pack. The interface with DEDPM, however, was poor. Similarly, composites made with Nicalon having 500 filaments/tow (fig. 13) did not exhibit layering. The Nicalon fiber is circular in cross-section, but ranges in diameter from 7 to 22  $\mu\text{m}$ , and does not close pack. Again, bonding between fiber and matrix was poor. This might be attributed to the sizing. Attempts to remove the sizing resulted in incomplete removal and fiber breakage on handling, and would likely require a continuous removal and winding operation to succeed.

## CONCLUSIONS

The current study has demonstrated that particulate filled, high char yield polymeric precursors can be processed at low temperatures to a ceramic matrix with <3 percent linear shrinkage, no large ( $>1 \mu\text{m}$ ) matrix pores and

minimal matrix cracking, thus requiring only a single impregnation and pyrolysis cycle.

Incorporation of large tows of small diameter fibers results in poor infiltration of particulates into the tow, residual thermal stresses evident on cross plying and low shear strength, which might be improved by changes in fiber shape and/or decreased bundle size, or in the choice of a smaller sized particulate filler or decreased particle loading.

Addition of wetting agent (A57) at low concentrations (0.5 percent) improved resin flow during fiber coating and inhibited spherulite formation on the fiber surface, improving prepreg handling. Microphase segregation is observed within the matrix as well as a decrease in strength of the matrix/particulate interface, influencing matrix modulus and composite shear behavior.

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TABLE I. - INFLUENCE OF A57 CONCENTRATION AND SOLVENT ON  
FLEXURAL STRENGTHS OF CELION 6000/DEDPM/SiC COMPOSITES

[Celion DEDPM/SiC/A57 3 Pt flexural strength 32:1.]

Solvent	A57	SiC/DEDPM, wt	Fiber tow size	$\sigma$ , MPa (ksi)	Failure mode
CH <sub>3</sub> CN	0	a2	6K	551 (80)	Shear
	.2	2	6K	834 (121)	Shear
	.42	2	6K	1068 (155)	Tensile/shear
	1.0	2	6K	723 (105)	Mixed mode
	1.0	a2	6K	620 (90)	Shear
	2.0	2	6K	482 (70)	Tensile/shear
DMF	.2	2	6K	868 (126)	Tensile/shear
	.42	2	6K	882 (128)	Tensile/shear
CH <sub>3</sub> CN	.5	1.6	3K	854 (124)	Tensile
	.5	2	3K	841 (122)	Tensile

<sup>a</sup>Coated both sides.

TABLE II. - TENSILE PROPERTIES OF CELION  
3000/DEDPM/SiC COMPOSITES

TENSILE PROPERTIES

Orientation	As fabricated		Pyrolyzed	
	$\sigma$ , MPa (ksi)	$\epsilon$ , %	$\sigma$ , MPa (ksi)	$\epsilon$ , %
0°	475 (69)	0.33	206 (30)	0.18
±45°	62 (9.1)	0.34	31 (4.5)	0.17

# MONOMERS

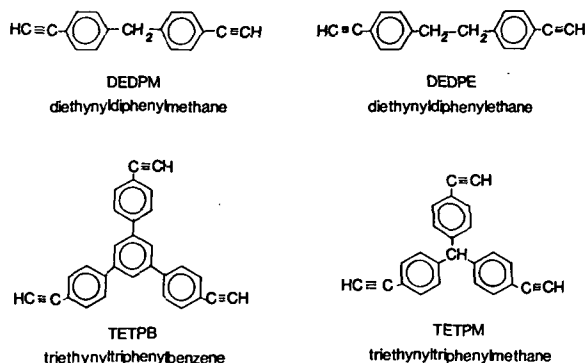


Figure 1. Structures of 4, 4'-diethynyldiphenylmethane (DEDPM) 4, 4'-diethynyldiphenylethane (DEDPE). 1, 3, 5-tris (4-ethynylphenyl) benzene (TETPB) and 4, 4', 4''-triethynyltri-phenyl methane (TETPM) monomers.

# CROSSLINKED HOMOPOLYMER OR COPOLYMER

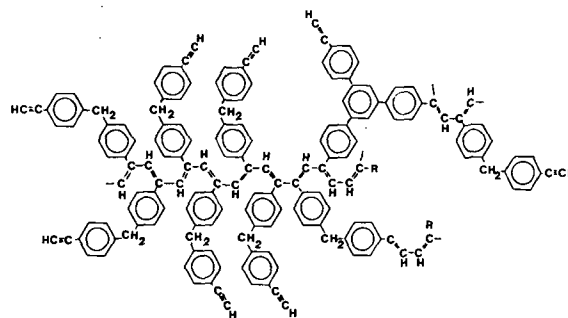


Figure 2. Schematic of cross-linked copolymer.

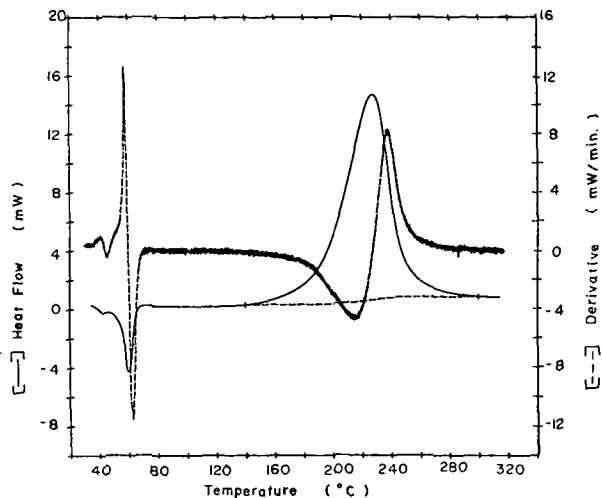


Figure 3. DSC trace of DEDPM cure obtained at a heating rate of 10°C/min.

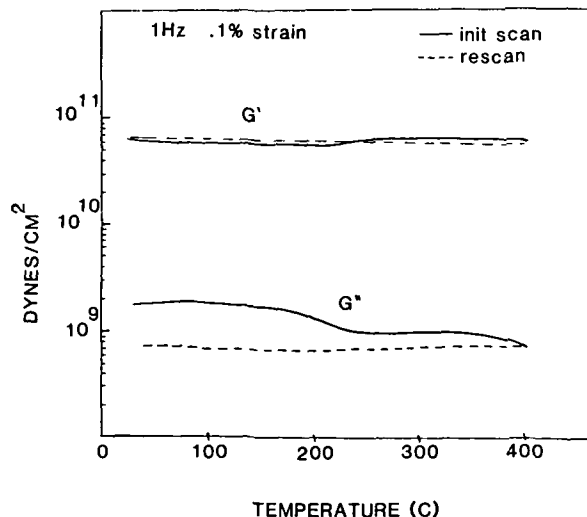


Figure 4. Shear moduli  $G'$  and  $G''$  obtained in forced torsion of Celion/DEDPM composite at 1 Hz.

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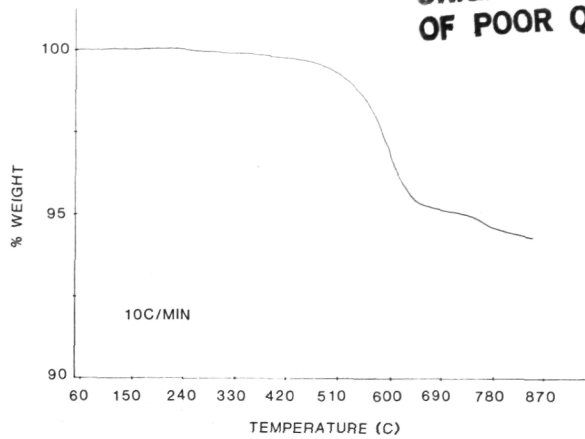


Figure 5. TGA trace of weight percent vs. temperature for a Celion 6000/DEDPM laminate heated at 10°C/min. in flowing nitrogen.

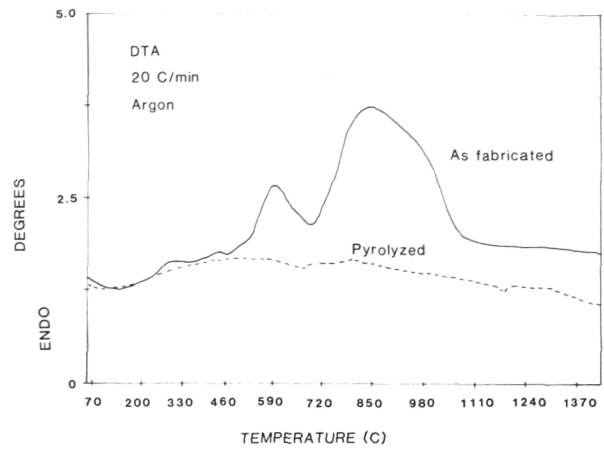
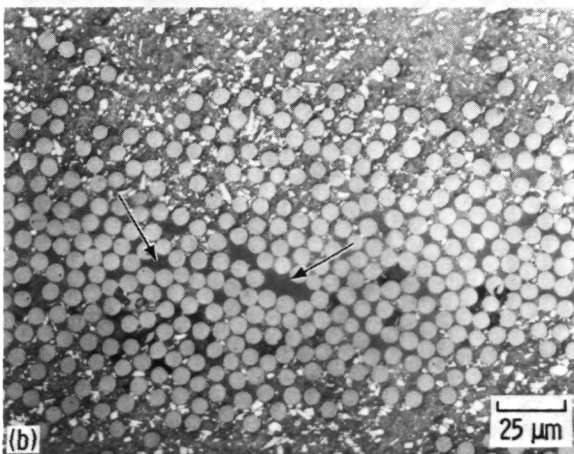
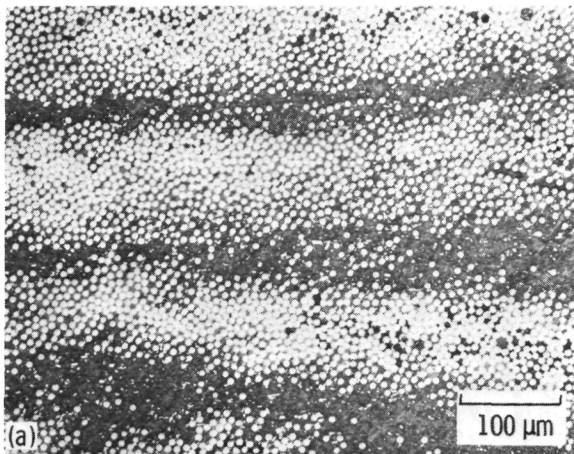
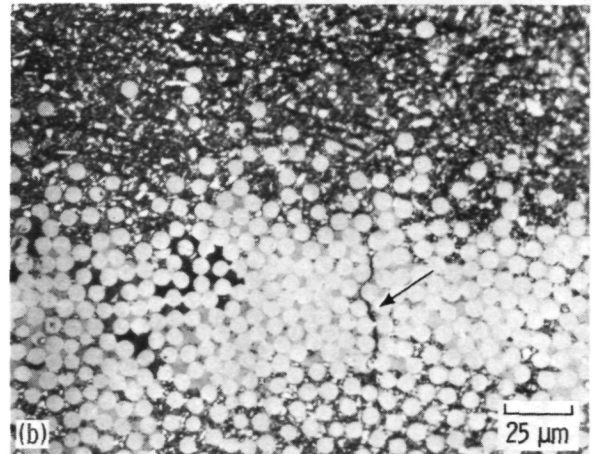
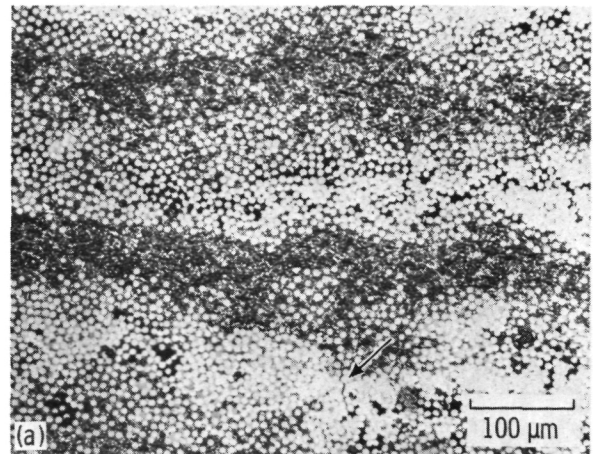


Figure 6. DTA scan of Celion/DEDPM/SiC composite; (-) as fabricated and (---) after postcuring and pyrolysis (3h at 600°C).



CS 85-0750

Figure 7. Microstructure of as fabricated Celion 6000/DEDPM/SiC composite. Arrows indicate areas of matrix devoid of SiC particles.



CS 85-0749

Figure 8. Microstructure of Celion 6000/DEDPM/SiC composite after pyrolysis in argon at 600°C for 3 h followed by heating in flowing argon at 1200°C for 1 h. Arrows indicate single matrix crack.

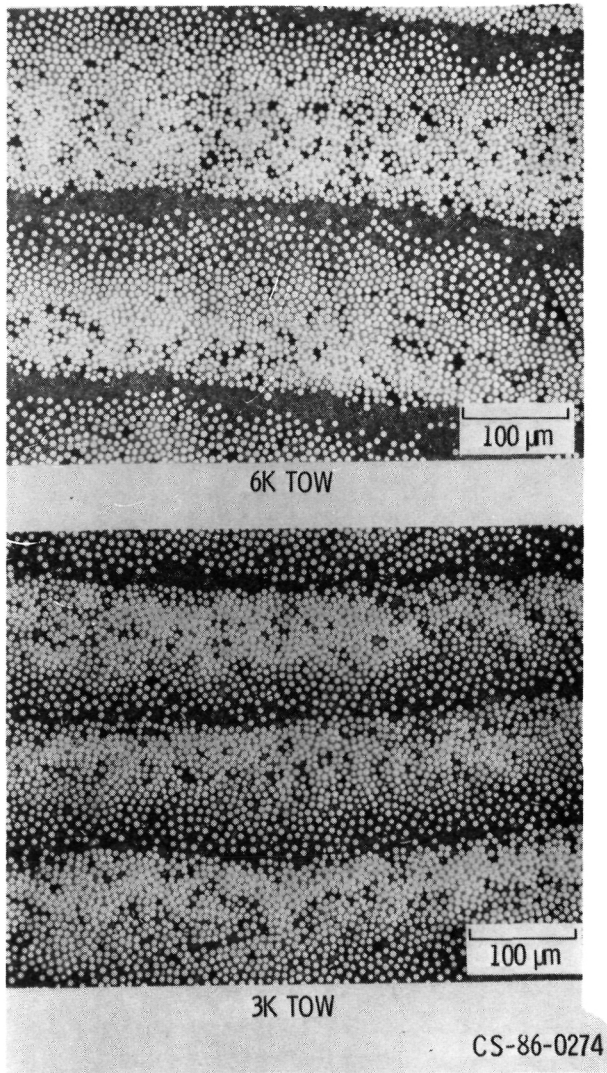


Figure 9. Comparison of Celion/DEDPM/SiC laminates fabricated from (a) 6K and (b) 3K filament tows.

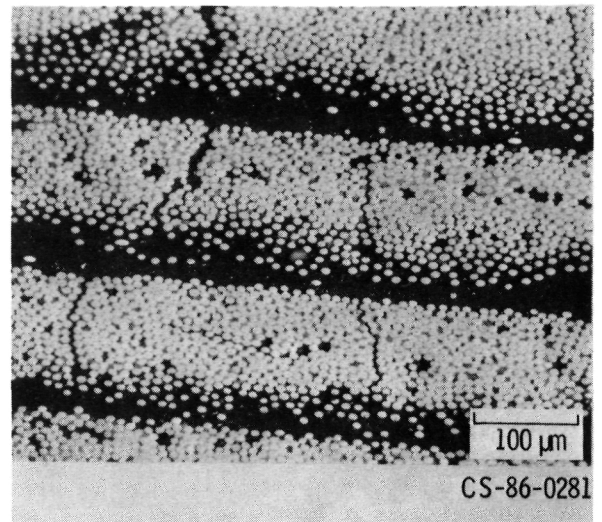


Figure 10. Microstructure of  $\pm 45^\circ$  Celion/DEDPM/SiC composite after pyrolysis.

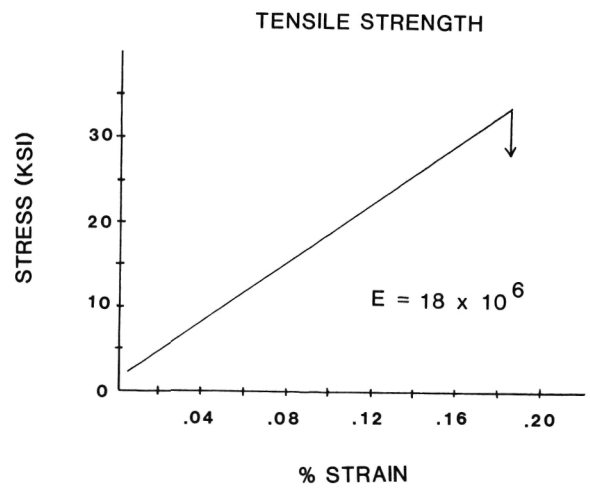


Figure 11. Stress-strain behavior at pyrolyzed Celion 3000/DEDPM/SiC tested in tension at  $0^\circ$  to the fiber axis.  $V_f \sim .6$ .

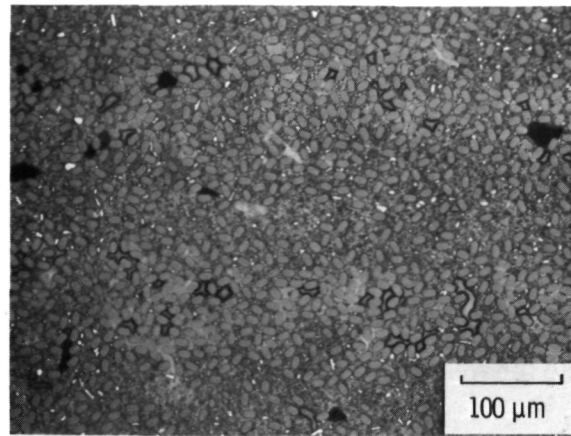


Figure 12. Microstructure of as fabricated Nextel/DEDPM/SiC composite.

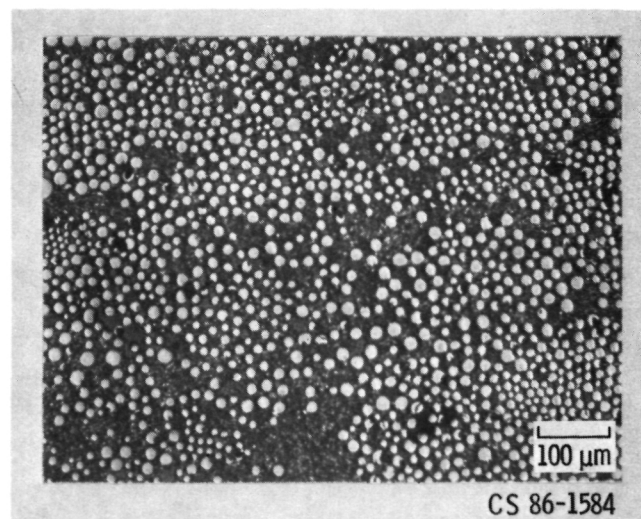


Figure 13. Microstructure of Nicalon/DEDPM/SiC composite.



1. Report No. <b>NASA TM-88812</b>		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle  <b>Carbon-Rich Ceramic Composites From Ethynyl Aromatic Precursors</b>				5. Report Date	
				6. Performing Organization Code  <b>506-43-11</b>	
7. Author(s)  <b>Frances I. Hurwitz</b>				8. Performing Organization Report No.  <b>E-3167</b>	
				10. Work Unit No.	
9. Performing Organization Name and Address  <b>National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135</b>				11. Contract or Grant No.	
				13. Type of Report and Period Covered  <b>Technical Memorandum</b>	
12. Sponsoring Agency Name and Address  <b>National Aeronautics and Space Administration Washington, D.C. 20546</b>				14. Sponsoring Agency Code	
15. Supplementary Notes  <b>Prepared for the Tenth Annual Conference on Composites and Advanced Ceramic Materials, sponsored by the American Ceramic Society, Cocoa Beach, Florida, January 19-24, 1986.</b>					
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17. Key Words (Suggested by Author(s))  <b>Ceramic composites; Ceramic fillers; High-char yield polymers</b>			18. Distribution Statement  <b>Unclassified - unlimited STAR Category 24</b>		
19. Security Classif. (of this report)  <b>Unclassified</b>		20. Security Classif. (of this page)  <b>Unclassified</b>		21. No. of pages	
				22. Price*	

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